PB86-108263

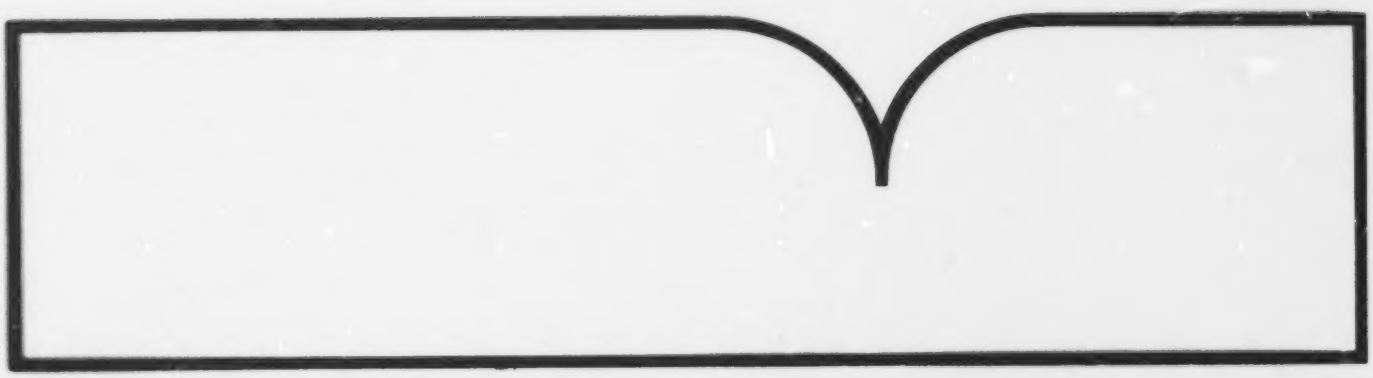
Primary Sulfate Emission Factors for the NAPAP (National Acid Precipitation Assessment Program) Emissions Inventory

Radian Corp., Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Sep 85



U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-108263

EPA/600/7-85/037
September 1985

PRIMARY SULFATE EMISSION FACTORS FOR THE NAPAP EMISSIONS INVENTORY

by

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Contract No. 68-02-3994

Work Assignment 5

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/7-85/037		

4. TITLE AND SUBTITLE	5. REPORT DATE
Primary Sulfate Emission Factors for the NAPAP Emissions Inventory	September 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
James B. Homolya	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Radian Corporation P. O. Box 13000 Research Triangle Park, North Carolina 27709	11. CONTRACT/GRANT NO. 68-02-3994, Task 5
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711	Task Final; 9/83 - 7/85 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is J. David Mobley, Mail Drop 61, 919/541-2612.

16. ABSTRACT The report gives results of an estimation of primary sulfate emission factors for use in the 1980 and 1985 National Acid Precipitation Assessment Program (NAPAP) emissions inventories. The estimates were developed from an assessment of existing measurements data for source categories including external combustion, chemical manufacturing, primary metals, wood products, mineral products, and petroleum refining. Initial elements of the assessment summarized primary sulfate formation mechanisms prevalent in combustion processes and reviewed the state-of-the-art methodology for primary sulfate sampling and analysis of source emissions. The Controlled Condensation System (CCS) was evaluated as the best primary sulfate emission measurement approach. CCS-derived measurement data were abstracted from an inventory of reports consisting of a variety of environmental assessment studies, field measurement evaluation experiments, and the U. S. / Canadian Work Group 3B inventory. The measurement data were then used to estimate primary sulfate emission factors for the corresponding source categories. Uncertainty estimates are given for each emission factor, and source categories are identified where data are either lacking or incomplete to permit the assignment of an emission factor.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Combustion	Pollution Control	13B	21B
Sulfates	Chemical Industry	Stationary Sources	07B	07A
Emission	Metals	Acid Rain	14G	11F
Precipitation	Wood Products	NAPAP	04B	11L
Acidity	Minerals		07D	08G
Measurement	Petroleum Refining			13H

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	56
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Primary sulfate emission factors were estimated for Task Group B, Man-Made Sources, of the National Acid Precipitation Assessment Program (NAPAP), for use in the 1980 and 1985 NAPAP Emissions Inventories. The estimates were developed from an assessment of existing measurements data for source categories including external combustion, chemical manufacturing, primary metals, wood products, mineral products, and petroleum refining. Initial elements of the assessment summarized primary sulfate formation mechanisms prevalent in combustion processes and reviewed the state-of-the-art methodology for primary sulfate sampling and analyses of source emissions. The controlled condensation system (CCS) method was evaluated as the best primary sulfate emission measurement approach. CCS-derived measurement data were abstracted from an inventory of reports consisting of a variety of environmental assessment studies, field measurement evaluation experiments, and the U. S./Canadian Work Group 3B Inventory. The measurement data were then used to estimate primary sulfate emission factors for the corresponding source categories. Uncertainty estimates are given for each emission factor and source categories are identified where data is either lacking or incomplete to permit the assignment of an emission factor.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

lb	-- pound (0.45359 kilogram)
ton	-- short ton (906.18 kilograms)
gal	-- U. S. gallon (3.7853 liters)
bbl	-- barrel (42 U. S. gallons)
MW	-- megawatt (1.02×10^8 kilograms-meters/second)

SECTION 1

PROJECT SUMMARY

INTRODUCTION

The National Acid Precipitation Assessment Program (NAPAP) was established by the United States Congress in 1980 to coordinate and expand research relevant to the problems posed by acid deposition in and around the United States. NAPAP is organized and managed through the Interagency Task Force on Acid Precipitation (ITFAP) and ten subordinate task groups coordinating specific technical areas of research. Task Group B: Man-Made Sources has the basic two-fold objectives of:

1. Providing an accurate and complete inventory of emissions from man-made sources believed to be important in acid deposition processes. The inventories are to be provided with adequate geographic, temporal, and sectoral resolution.

2. Providing models which predict how acidic and acid-presursor emissions may be altered by factors such as economic growth, fuel supply, emissions regulation, and control techniques. The models are to have the capability to permit the calculation of alternative control strategies.

Task Group B has prepared a NAPAP Emissions Inventory Implementation Plan[1] which is designed to address the needs of the NAPAP research programs being conducted by the other nine task groups within ITFAP. In general, the emissions inventory needs of these various task groups can be summarized in two categories:

1. Detailed, multicomponent point and area source disaggregated inventory for defined annual base years to support the development and testing of atmospheric transport and transformation models to predict acid deposition.

2. Retrospective inventory summaries of acidic and acid-presursor emissions over the past eighty years to support historical analyses of materials damage and to aid in developing policy assessments.

The modeling activities presently envisioned by NAPAP include the utilization of both Eulerian and Lagrangian Acid Deposition Models. Eulerian model development is being directed by the EPA/ORD Environmental Sciences Research Laboratory which is supporting the development of a modeling approach similar to the Northeast Regional Oxident Study (NEROS) Model. Lagrangian modeling involves the use of existing models developed by EPA and others. Given the general emissions inventory requirements of each modeling approach and the needs of those task groups dealing with assessments and historical analyses, the NAPAP Emissions Inventory Implementation Plan identified that the level of temporal, spatial, and sectoral resolution to be contained in the NAPAP Emissions Inventory. The highest level of detail in the NAPAP Inventory must be directed to the requirements of the Eulerian Model.

Emissions inventory development is geared to provide data for both the 1980 and 1985 base years which have been targeted for modeling studies. The 1980 inventory contains emissions for SO_2, NO_x, VOC, primary sulfate, NH_3, CO, and particulate matter.

APPROACH

This report summarizes an analysis of existing data on primary sulfate emissions from a variety of source categories and presents a tabulation of primary sulfate emission factors appropriate for use with the NAPAP Emissions Inventory. This analysis also identified areas where data are either lacking or incomplete to permit the assignment of an emission factor. The study does not address the relative importance or abundance of primary sulfates in the atmosphere compared to "secondary" sulfate derived from the atmospheric transformation of sulfur dioxide. These types of assessments require extensive emissions and air quality measurements which must be evaluated through the use of complex transport and transformation models.

Prior to the current need for NAPAP Task Group B to inventory primary sulfate emissions, two different environmental program activities have included assessments of primary sulfate emission factors for use in emission inventory development. The EPRI-sponsored sulfate regional experiment (SURE) program summarized existing experimental measurements data on primary sulfates and recommended generalized emission factors for a large number of source

categories. For the most part, many of the factors were based upon an extrapolation of a limited data set for uncontrolled fossil fuel combustion sources along with data contained in the EPA Emission Factor Guidelines (AP-42) for sulfuric acid manufacturing to inventory the range of source classification coded point and area sources in the midwestern and northeastern United States and southeastern Canada. At that time, primary sulfate field measurement methodology was under development by EPA. Consequently, much of the existing data in the literature were qualified by the uncertainty of the sampling and analysis procedures. In fact many of the available field measurement data were obtained for the purpose of method development with the attendant problem that few critical supporting measurements were taken to permit the proper calculation of emission factors.

More recently, the United States/Canada Work Group 3B (WG 3B) prepared an emissions measurement report in accordance with the Memorandum of Intent on Transboundary Air Pollution of August 1980. The report included an estimate of United States and Canadian primary sulfate emissions using emission factors obtained from a study of available data conducted by the Ontario Research Foundation. Those emission factors were abstracted from similar open literature sources used for preparation of the SURE Inventory along with unpublished emissions data from Canadian measurements. Emission factors were reported for uncontrolled fossil fuel combustion sources as well as for primary metal smelters. Measurements data for smelters were acquired from tests in Canada using a variety of sampling and analysis methods.

Since the preparation of the SURE and WG 3B inventories, several developments have occurred regarding primary sulfate emission measurements. The first major development has been the acceptance of a standard sampling and analysis procedure for sulfate emission assessment. The source emission measurement technical community now agree that the controlled condensation sampling (CCS) procedure is the best approach for the determination of H_2SO_4, and particulate sulfate emissions from stationary sources. Although this acceptance does not invalidate previous source measurements using methodology available at the time, the integration of CCS into field measurement programs conducted by EPA and other has afforded the opportunity to assess the general consistency of sulfate emission measurements conducted at various point sources within given source categories.

As a result of a series of environmental assessment studies conducted by the EPA's Industrial and Environmental Research and Environmental Sciences Research Laboratories, several field programs included detailed primary sulfate emission measurements taken at both uncontrolled and SO_2-controlled utility and industrial sources utilizing a variety of fuels. The importance of sulfate emission measurements for scrubber-equipped sources became apparent after researchers discovered that scrubbers removed proportionately less sulfate than SO_2 from flue gases.

Therefore, the objective of this report is to summarize the current body of sulfate emissions data. This investigation consisted of four major activities including:

1. a summary discussion of primary sulfate formation mechanisms thought to be prevalant in combustion processes;
2. assessment of the state-of-the-art methodology for primary sulfate sampling and analysis of source emissions;
3. review of the SURE and WG 3B primary sulfate emission inventories; and
4. collection, review, and calculation of primary sulfate emission factors derived from additional field studies not included in the SURE and WG 3B inventories.

RECOMMENDED PRIMARY SULFATE EMISSION FACTORS FOR THE NAPAP INVENTORIES

Primary sulfate emission factors recommended for use in the NAPAP Emissions Inventories are given in Table 1. The factors are reported for a number of source classification codes (SCCs) based on an analysis of available data. Most of the current data set is for fossil fuel combustion in the industrial and utility sectors. The emission factors have been calculated to a normalized Emissions Information System (EIS) format as:

Sulfate emissions per SCC unit = (Emission factor x percent sulfur content of fuel)

The emission factors given in Table 1 reflect sulfate emitted as $SO_4^{=2}$ based upon chemical analyses of source test samples. The source descriptions and fuel sulfur contents for fossil fuel combustion are given in Section 4. Emission factors for fuel sulfur contents other than those given in Section 4

TABLE 1. PRIMARY SULFATE EMISSION FACTORS FOR NAPAP EMISSIONS INVENTORY

Source category	NEDS Source classification code (SCC)	Control device	Primary sulfate emission factor	Reference	Uncertainty range*
Electric Utilities - External Combustion					
Eastern bituminous coal	1-01-002	ESP	0.385 lb/ton	25, 28	A
		ESP and FGD	0.250†	25, 28	C
Western bituminous coal	1-01-002	ESP	1.290	26, 27	B
		ESP and FGD	0.761		C
Lignite	1-01-003	ESP	1.951	26	C
Residual oil (>1% sulfur content)	1-01-004	Fuel oil additive	5.439 lbs/1,000 gallons	29	B
Industrial - External Combustion					
Eastern bituminous coal	1-02-002	Multiclones	2.646 lbs/ton	30, 31	B
		Multiclones and FGD	0.462	30	C
Residual oil	1-02-004	Multiclones	5.296 lbs/1,000 gallons	30	D
		Multiclones and FGD	2.616	30	D
Commercial/Institutional - External Combustion					
Residual oil (<1% sulfur content)	1-03-004	Fuel oil additive	25.07 lbs/1,000§ gallons	32	C
Space Heating - External Combustion					
Distillate oil	1-05-001-05	None	5.65 lbs/1,000 gallons	34	C
Industrial Process - Chemical Manufacturing					
H_2SO_4-contact process	3-01-023	Demister	0.100 lb/ton acid produced	4	B
Industrial Process - Primary Metals					
Primary copper smelters	3-03-005-1		22.5 lbs/ton concentrated ore	4	C
	3-03-005-2		1.08	4	C
	3-03-005-3		5.76	4	D
	3-03-005-4		15.66	4	D

(continued)

TABLE 1. (continued)

Source category	NEDS Source classification code (SCC)	Control device	Primary sulfate emission factor	Reference	Uncertainty range*
Industrial Process - Primary Metals (Cont'd)					
Primary zinc smelters	3-03-030		55.5 lbs/ton processed	4	D
Primary aluminum smelter	3-04-001		0.5% of SO_2	4	D
Iron production	3-03-008		2.0% of SO_2	4	D
Coke	3-03-003		0.320 lb/ton coal charged	4	D
Industrial Process - Wood Products					
Kraft pulp mill	3-07-001		#	4	C
Sulfite pulp mill	3-07-002		**	4	C
Wood/bark waste	1-02-009	Multiclones	3.6 lbs/ton bark	33	D
Industrial Process - Mineral Products					
Cement manufacturing	3-05-006 and 3-05-007		††	4	D
Gypsum manufacturing	3-05-015		§§	4	D
Industrial Process - Petroleum Industry					
Fluid crackers	3-06-002	ESP	15.0 lbs/1,000 barrels oil	4	C
Sulfur recovery Claus plants	3-01-032		2.8 lbs/ton produced	4	C

* Estimated emission factor uncertainty. Assumes that 90% of the values for an individual source lie within the mean uncertainty estimates. Corresponding values are: A = ±10%; B = ±25%; C = ±50%; D = ±75%, and E = 100%.

† Emission factor based on average sulfate scrubbing efficiency of 35%.

§ Emission factor applicable only to low sulfur content (0.3% S) residual fuel oil.

Total sulfate emissions for kraft pulp mills estimated as 85% of NEDS total particulate emissions from kraft recovery boilers (see Reference 36).

** Total sulfate emissions from sodium-base sulfite mills estimated as 70% of NEDS SO_2 emissions; for calcium-base sulfite mills estimated as 25% of NEDS SO_2 emissions (see Reference 36).

†† Total sulfate emissions from cement kilns estimated as 5.6 lbs/ton of cement on an uncontrolled basis. Average particulate control efficiency from NEDS data assumed to apply in order to calculate actual emissions (see Reference 36).

§§ Total sulfate from gypsum plants estimated as 56% as NEDS actual particulate emissions (see Reference 36).

can only be estimated since the dependence of primary sulfate emissions on fuel sulfur content had not been studied in detail. In fact, the limited data available suggest that sulfate emissions can be markedly affected by other parameters such as furnace oxygen levels and trace element content of the fuel. For source categories other than fossil fuel combustion, sulfate emission factors are reported in standard SCC units or as percentages of mass particulate emissions.

The calculation of specific primary sulfate emission factors were based on the following heirarchical selection process.

1. Where available, all field measurements using the CCS procedure were considered as the prime data set.

2. Sulfate emission assessments were aggregated for different point sources within the same source category only if fuel composition and emission controls were similar.

3. Emissions data acquired through the use of methods other than CCS were included only if multiple measurements yielded data with minimal scatter.

Therefore, the primary sulfate emission factors summarized in Table 1 are representative of the current emissions data base and reflect the WG 3B emission factors calculated for source categories other than fuel combustion.

There are a number of source categories for which no experimental field data exist. At present, the only alternative to an emission factor for the NAPAP Emission Inventory is the assignment of an "assumed" factor already contained within the source allocation codes for the Regional Model Data Handling System (RMDHS). However, most of the regional mass emissions of primary sulfates should occur from those source categories for which emission factors have already been substantiated (utility and industrial fossil fuel burning). The best approach to improving the NAPAP Emissions Inventory sulfate component may be an expanded field measurement activity which focuses on those source categories which have not been sufficiently characterized but are potentially significant contributors to regional emissions. Improvements are needed in the data base for low sulfur residual oil-fired industrial and commercial boilers. Field measurements using the CCS procedure are recommended for this source type which is a significant source of sulfur

emissions in major metropolitan areas in the eastern United States. In addition, sulfate emissions from the pulp and paper industry need further characterization given the large preliminary emission factors reported by WG 3B. Pulp mill operations are concentrated in the acid deposition sensitive Northeast and represent a major SO_2 and particulate source contributor in the southeastern United States.

SECTION 2

FORMATION OF PRIMARY SULFATES IN COMBUSTION SOURCES

Sulfur present in fossil fuels is emitted to the atmosphere mainly as sulfur dioxide (SO_2). However, some of the sulfur is oxidized further in the combustion process and is emitted in a variety of forms, collectively known as "primary sulfates". These forms include gaseous sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4), sulfuric acid mist, and metallic sulfates (MSO_4, where M may be metal or ammonium ions). Secondary sulfates are formed in the atmosphere by the oxidation of some of the emitted SO_2. Some SO_2 and sulfates, both primary and secondary, are returned to the earth by wet or dry deposition. Others remain in the atmosphere and may be transported far from the emission source. These atmospheric sulfates form ambient aerosols - stable mixtures of gases, liquid droplets, and particles.

The largest source of primary sulfate emissions (PSE) appears to be from the combustion of coal and oil. The amount of primary sulfates emitted from a particular combustion source is dependent on a great number of factors. Among these are fuel type and composition, equipment type and design, operating parameters, and emission controls.

FUEL CHARACTERISTICS

A significantly higher conversion of fuel sulfur to primary sulfates occurs during oil firing as compared to coal firing. In general, the fraction of fuel sulfur emitted as primary sulfates has been found to be related to the metals content of the fuel as well as the amount of excess air used for combustion. It is believed that, among other factors, the relatively higher vanadium and nickel content of residual fuel oil contributes to the higher conversion of fuel sulfur to sulfate.

Several other fuel characteristics have an effect on PSE. Table 2 shows some of the properties of coal and oil which are important in assessing the potential of the fuel to form primary sulfates when burned.

TABLE 2. COMPARISON OF FUEL CHARACTERISTICS

	Coal	Fuel oil
Burn rate	Relatively slow	Relatively fast
Ash content	5 to 15%*	0.01 to 0.20%
Principal metals	Si, Al, Fe, Ca	Mg, Na, V, Ni
Minor metals	Mg, Na, K	Ca, Fe, Al
Sulfur content	0.2 to 7%*	0.1 to 4%

* Weight percent, dry basis.

Characteristics of Coal

Coal is a slow-burning fuel, which results in a lower flame temperature than is achieved with oil firing. Relatively low flame temperatures lessen production of SO_3 formed in the flame zone by the combination of SO_2 with atomic oxygen.

The principal metals which typically constitute coal ash are silicon, aluminum, iron, and calcium, which are usually present in the oxide form. Magnesium, sodium, and potassium are usually present, but in much smaller amounts. Certain coal ashes such as those formed from lignite combustion are basic, so some of the acid formed during coal combustion is neutralized in the flue gases by the large quantity of ash produced. The high ash content and slow burning properties of the fuel tend to make coal-fired boilers emit less of the fuel sulfur as SO_3 and H_2SO_4 than oil-fired boilers of comparable size.

Although the sulfur content of coal is in many cases higher than fuel oil, some of the sulfur present in coal is trapped in bottom ash which is not emitted to the atmosphere. In any case, the sulfate content of bituminous coal ash emitted to the atmosphere is less than 1.5 percent as $SO_4^=$.

Properties of Fuel Oil

The low ash, fast burning properties of fuel oil favor formation of primary sulfates during oil firing. In particular, the ability of some of the principal metals in oil ash to catalyze the formation of SO_3 in the combustion process contributes to increased sulfate emissions. Table 3 summarizes the effects on PSE of different fuel oil characteristics.

TABLE 3. EFFECTS OF FUEL OIL CHARACTERISTICS ON PSE

Increasing. . .	Causes. . .
Percent V in oil	Increased SO_3, H_2SO_4 and MSO_4 emissions
Other metals in oil	Increased MSO_4 emissions
Percent S in oil	Increased SO_3, H_2SO_4 and MSO_4 emissions

COMBUSTION PROCESSES

Specifics of the combustion process, such as equipment type and design, operating parameters, and emission controls, can affect the quantity of PSE. There are several possible mechanisms by which primary sulfates are believed to form in combustion processes.

Primary Sulfate Formation Mechanisms

Sulfates are formed in combustion processes in both the flame region and downstream in the heat transfer section. The proportions of total PSE formed in each region are not known, and probably vary from process to process. Primary sulfates are formed by oxidation of SO_2 to SO_3, hydration of SO_3 to H_2SO_4, corrosion of boiler internals by H_2SO_4, and conversion of metallic oxides in ash to particulate sulfates.

In combustion flames, the predominant sulfate formation mechanism is reaction of SO_2 with molecular oxygen to form SO_3.[5] In the adiabatic flame region, peaks of SO_3 can occur which coincide with peaks of O atom concentration resulting from CO combustion. However, as combustion reactions reach equilibrium, SO_3 concentrations drop to less than 1 ppmv, thus only a small portion of emitted SO_3 is formed in the flame region.

As combustion products are cooled by radiative and conductive heat transfer in the post-flame region, O atom concentrations exceed O-O_2 equilibrium. This causes an increase in SO_3 concentration above SO_2-SO_3 equilibrium levels at the flame temperature. With further cooling, production of O atoms ceases. Oxygen molecules form from O atoms, which are rapidly depleted by this reaction. This depletion prevents formation of more SO_3, the concentration of which remains at a superequilibrium level above that normally expected at the flame temperature.

The final SO_3 concentration depends on O_2 concentration, cooling rate, and the location and rate of mixing of excess air. Only fuel-rich combustion (zero percent excess O_2) can prevent SO_3 formation by flame processes. For fuel-lean combustion, SO_3 concentration increases nearly linearly with O_2 concentration in the range zero to 3 percent excess O_2. In excess of 3 percent O_2 above stoichiometric, only slight increases in SO_3 concentration are noted. Decreasing the level of excess O_2 in the combustion process has been shown to decrease sulfate emissions, but this practice is not feasible for all systems.

The rate of cooling of combustion gases in the temperature range 1,650°C to 820°C is another parameter affecting SO_3 formation in the post-flame region. An increase in SO_3 concentration occurs when combustion products are rapidly cooled in the heat transfer section of the boiler. Rapid cooling rates result in superequilibrium O atom concentrations and the production of more SO_3, the concentration of which increases with increasing rates of cooling. Altering the cooling rate of combustion gases in existing equipment would involve major modifications. New sources designed for slower cooling rates would probably be less energy efficient overall than current designs.

Proper staging of excess air addition after fuel-rich combustion can minimize SO_3 formation. This technique has been used to reduce NO_x emissions from combustion sources. However, staged-air mixing to high excess O_2 levels

in the range 1,090°C to 1,650°C must be avoided, since in this range excess O_2 causes high O atom concentrations and results in higher SO_3 levels than occur with normal unstaged combustion.[6] Further modeling and experimental work is needed to determine whether staged air addition can be effectively used to limit SO_3 formation.

The importance of catalysis in the oxidation of SO_2 to SO_3 has been studied by many investigators. Many different substances have been shown to have a catalytic effect on the reaction, and have thus been implicated as contributing to increased PSE. Hedley and Cullis[7] and Mulcahy[8] have discussed the homogeneous catalysis of SO_2 oxidation by NO_2, and Levy and Merryman[9] demonstrated an increase in SO_3 when the oxidant in combustion was switched from O_2-Ar to O_2-N_2.

Heterogeneous catalytic oxidation of SO_2 by metals, metal oxides, and soot suspended in the stream of combustion gases or deposited on boiler internal surfaces can occur to substantially increase PSE. One of the best catalysts for conversion of SO_2 to SO_3 is V_2O_5. Residual fuel oils from Venezuela and the Middle East contain significant amounts of vanadium, which is liberated as V_2O_5 during combustion. Vanadium catalysis has been noted often in the literature.[10,11,12,13] At high relative humidities, Fe_2O_3[14,15,16] and MnO_2[15,17] are also strong catalysts. The major constituents of coal fly ash, SiO_2 and Al_2O_3, are only weak catalysts. Soot (carbon) has been reported to catalyze SO_2 oxidation[18] but data are mainly qualitative, and little is known of the importance of particle characteristics or temperature on the catalytic action.

Sulfuric acid is formed by reaction of SO_3 with water vapor in combustion product gases. This H_2SO_4 can adsorb on ash or soot particles, condense on cooler parts of the combustion equipment, or be emitted to the atmosphere as a mist. The SO_3-to-H_2SO_4 conversion is temperature- and moisture-dependent. For example, at a flue gas moisture level of eight volume percent, the following observations can be made: (1) above 370°C essentially all the SO_3 is in the vapor phase; (2) from 370°C to 205°C SO_3 reacts with water vapor to form H_2SO_4 vapor; and (3) below 205°C, H_2SO_4 condensation occurs and the gas stream consists of an equilibrium mixture of H_2SO_4 liquid aerosol and H_2SO_4 vapor. Because of this integral relationship between SO_3 and H_2SO_4, the two

are often referred to collectively as SO_3/H_2SO_4. As the temperature of the flue gas decreases, it approaches the acid dewpoint, which is a function of SO_3/H_2SO_4 concentration. When flue gas temperature reaches the acid dewpoint (at a given SO_3/H_2SO_4 concentration), concentrated H_2SO_4 condenses on air heaters, ductwork, fly ash collectors, and stacks. The resulting corrosion cycle can pose a serious problem and can exacerbate primary sulfate emissions as described below.

The formation mechanism for metallic sulfates (MSO_4) is subject to some debate. Some MSO_4 is probably formed by conversion of metal oxides in ash to sulfates by the action of adsorbed H_2SO_4. Additionally, sulfuric acid condensed on boiler internals can react with the iron (and possibly with other constituents of metallic alloys such as Ni, Cr, Mo) in the system to form corrosion products. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), a corrosion product, can further react with SO_2 and oxygen in the flue gas to yield highly corrosive ferric sulfate ($Fe_2(SO_4)_3$). Below pH 3, the latter will attack boiler metal, producing more ferrous sulfate, and beginning the corrosion cycle again.[16] Another suggested mechanism, of which little is known, is direct gas-to-particle conversion of SO_2 and atomic or molecular oxygen to particulate sulfates.

Process Differences

The amount of PSE from combustion sources can be affected by several system design parameters, including fuel type, source type, and equipment configuration. With few exceptions, oil-fired sources are not equipped with emission control systems. In the late 1960's, many existing sources converted to oil from coal to comply with emissions regulations for SO_2 and particulates. The mechanical collectors used for particulate control at these sources are ineffective for removing significant quantities of ash from oil firing, and thus fail to substantially mitigate PSE. Recently, large oil-fired sources have successfully used MgO-based fuel additives, which decrease PSE from these systems.

In contrast to oil-fired sources, coal-fired sources often employ both particulate and SO_2 control. Electrostatic precipitators have been shown capable of removing in excess of 50 percent of the primary sulfates generated

from coal combustion.[18] Flue gas desulfurization systems not only remove SO_2 from stack gases, but also trap some of the primary sulfates from coal firing. Among coal-fired sources, burner type can affect the characteristics of PSE. For example, pulverized coal firing emits particles which are, on average, smaller than those emitted from stoker-fired units.

SECTION 3

REVIEW OF PRIMARY SULFATE EMISSION MEASUREMENT METHODOLOGY

The accuracy of primary sulfate emission factors depends on the ability to accurately measure and characterize sulfate emissions. This discussion includes descriptions and evaluations of the various method used to characterize PSE from combustion sources.

The measurement of primary sulfate emissions in combustion sources has been conducted on an extractive basis. The two most commonly known methods for measuring SO_3/H_2SO_4 are the collection of the acid by absorption and by selectively condensing the acid in a temperature-controlled condenser. Both of these methods, which involve the extraction of the sample, have critical parameters which affect the accuracy of the emission measurement. The first element, which is common to all such extractive sampling of flue gases, is the separation of the particulate matter from the gaseous portion of the sample gas. If one is to speak of acid as a separate species from particulate sulfate, this separation must be achieved prior to the collection and measurement method. This separation is ordinarily attempted by placing some type of filter on or in the sample entrance end of the probe. The potential difficulty with the probe filter not only involves the efficiency with which the separation can be achieved, but may well involve the oxidation of SO_2 either on the filter material itself or on the particulates which accumulate on the filter surface during sampling. For the acid collection after this separation, problems have also been proposed both with respect to the oxidation of SO_2 in the absorption medium as well as acid mist collection efficiency for both methods.

Extractive sampling of flue gases for the purpose of measuring SO_3 and H_2SO_4 can be summarized by stating that the accuracy of the measurement is contingent on how well the separation can be achieved as well as how efficiently the acid can be collected.

ABSORPTION SYSTEMS

A number of investigators have developed some form of the selective absorption procedure. In selective absorption, the gas stream enters an ice cooled bubbler containing a solution of 80 percent isopropyl alcohol (IPA), which absorbs the H_2SO_4 and passes most of the SO_2. The SO_2 is absorbed downstream in H_2O_2 bubblers and oxidized to sulfate. There is evidence that IPA prevents the oxidation of SO_2, so that theoretically absorbed SO_2 can be purged later from the IPA bubbler using SO_2-free air (normally ambient air). This procedure is the basis for the standard EPA Method 6.

Several investigators, recognizing the need to collect both metallic sulfates (MSO_4) and H_2SO_4, have extended the M6 system by the addition of a glass wool plug in the probe. This modified Method 6 (MM6) procedure is capable of partially separating MSO_4 from the gaseous H_2SO_4 (including SO_3), and has been used extensively to measure PSE. However, a laboratory study has shown that the alkaline nature of the glass plug actually favors capture of a major portion of the sulfuric acid in the emission stream. This results in an incomplete separation of H_2SO_4 and MSO_4.

The operation of the MM6 train is similar to EPA Method 6. At the end of the test, the probe is removed from the stack and any SO_2 dissolved in the IPA impinger is purged with clean ambient air. The probe plug and probe are either washed with H_2O or rinsed directly with 80 percent IPA and titrated. The IPA bubbler, plug, and H_2O_2 impingers are treated in the same fashion as the EPA M6 procedure.[19]

The primary purpose in the design and operation of the MM6 train was to efficiently trap sulfates (sulfuric acid and metallic sulfates) and SO_2. Data reported from this train is typically divided in water soluble sulfate (H_2SO_4, MSO_4) and SO_2. Other selective absorption methods include the standard EPA Method 8[20] and the Shell-Emeryville method.[21]

CONDENSATION SYSTEMS

Development of the controlled condensation system (CCS) is generally attributed to the work of Goksoyr and Ross.[22] In the controlled condensation approach, H_2SO_4 is separated from the gas stream by cooling the flue gas in a

coil below the dew point for H_2SO_4 but above the dew point of H_2O. The resulting H_2SO_4 aerosol is either collected on the walls of the cooling coil or on a back-up frit. The H_2O and SO_2 passes from the controlled condensation coil (CCC) to an impinger system where the SO_2 is trapped and oxidized in impingers containing dilute H_2O_2. Laboratory studies have found the precision and accuracy of controlled condensation to be ±6 percent in synthetic gas streams. Recognizing the need to improve the particulate removal capability of the controlled condensation approach, an improved filtration system was designed, and extensive field testing [22,23,24] was conducted to determine the effect of operating parameters. The use of the controlled condensation system is considered to be the best state-of-the-art approach for conducting primary sulfate emission measurements at fossil fuel combustion sources.

SECTION 4

REVIEW OF AVAILABLE PRIMARY SULFATE EMISSION FACTOR DATA BASES

A limited number of previous emissions inventory development programs have considered inclusion of primary sulfates as a non-criteria pollutant to be inventoried. Two separate activities which were identified are:

1. Emissions Inventory for the SURE Region;[3] and
2. Work Group 3B Emissions Inventory.[4]

In this section, the sulfate components of each inventory are reviewed for applicability of emission factors to the NAPAP Emission Inventory.

Several recent test reports were identified which either describe specific primary sulfate emission assessments or included a limited number of primary sulfate measurements as part of a comprehensive environmental emissions assessment study. Each test report has been reviewed and is summarized. A primary sulfate emission factor has been calculated and listed for each source/fuel/emissions control element discussed in the test reports. Although each emission factor presented is based on multiple measurements at each source, the data sets still require more intensive study to assess the uncertainties of the source-categorized factors.

PRIMARY SULFATE EMISSION FACTORS FROM THE SURE EMISSIONS INVENTORY[3]

The Electric Power Research Institute sponsored an extensive study which was aimed at defining the mechanisms that link emissions to ambient concentrations of sulfur dioxide and sulfates and at the development of an air quality model that could relate emissions to ambient concentrations. The monitoring and modeling study (the Sulfate Regional Experiment - SURE) involved the development of a detailed emissions inventory for all man-made stationary sources of emissions and surface transportation emissions focused on the eastern United States and parts of southern Canada.

Included in the inventory are emission estimates for SO_2 and primary sulfates. Major problems were encountered in acquiring valid and reasonably accurate data for sulfate because of the limited amount of available test data. Those data which were available for major sulfate source emissions such as fossil fuel combustion were acquired by a variety of sampling and analysis methods which had not been validated. Based on available data, the following emission rates were applied to sulfur emissions from boilers.

- Coal-fired boilers. SO_x equivalent to 95 percent of fuel sulfur, SO_4 equivalent to 1.0 percent of SO_x, and SO_2 equivalent to 99.0 percent of SO_x.
- Oil-fired boilers. SO_x equivalent to 94 percent of fuel sulfur, SO_4 equivalent to 6.0 percent of SO_x emissions, and SO_2 equivalent to 94.0 percent of SO_x.

Sulfate emissions from sulfuric acid plants were estimated at 20 percent of the SO_x emissions based on EPA estimates contained in AP-42. For mobile source gasoline combustion the limited data available on sulfate emissions from catalyst-equipped vehicles reported levels which are insignificant. The sulfate emissions from overall gasoline combustion was estimated to be about 4 percent of the SO_x.

Sulfate emissions data for other sources were unavailable. Therefore, the following general assumptions were made.

- For those source categories using fossil fuel combustion for process heat or steam, the sulfate emission factors for boilers were used.
- Sulfate emission estimates for sulfuric acid production were used for those source categories which used sulfuric acid in various product manufacturing schemes according to the consumption of sulfuric acid in the process.
- For those source categories which could not be included in the two previous general classifications discussed above, it was arbitrarily assumed that SO_4 emissions were equivalent to 0.5 percent of the SO_x emissions.

Primary sulfate allocation factors were then assigned to the entire array of NEDS Source Classification Codes (SCC), as appropriate. As a result of the extensive extrapolation of a limited number of source measurement data sets to a wide range of SCCs, there is some question regarding the uncertainties of sulfate emission estimates for a specific SCC.

PRIMARY SULFATE EMISSION FACTORS UTILIZED BY WORKING GROUP 3B[4]

An emissions measurement report was prepared by the U.S./Canada Work Group 3B on emissions, costs and engineering assessment in accordance with the Memorandum of Intent on Transboundary Air Pollution concluded between Canada and the United States on August 5, 1980. As part of this activity, preliminary estimates of primary sulfate emissions for the U.S. were developed for the calendar year 1980. The work group concluded that the draft report Anthropogenic Sources and Emissions of Primary Sulfates in Canada, prepared for Environment Canada by the Ontario Research Foundation, contained the most complete collection of information on primary sulfate emission factors. The emission factors contained in this report were based upon information obtained from Canadian sources, open technical literature, EPA reports, and EPA data bases. Many of the references cited for the emission factor development were identical with those used for the preparation of the EPRI-sponsored Emissions Inventory for the SURE Region. Table 4 summarizes the emission factors used to prepare the WG 3B primary sulfate emissions estimates. For consistency and intercomparison with similar data, the factors have been recalculated and expressed in units appropriate for NAPAP inventory development.

EMISSION CHARACTERIZATION OF MAJOR FOSSIL FUEL POWER PLANTS IN THE OHIO RIVER VALLEY[25]

The purpose of the study was to characterize the atmospheric emissions from five major coal-fired power plant units in the Ohio River Valley between Portsmouth, Ohio, and Louisville, Kentucky. This characterization provided data that are representative of the boiler fuel emission control combinations of the current power plant population scheduled to go on line before the end of 1983. The selection criteria for the units to undergo testing included the following:

- size of unit;
- age and condition of unit;
- furnace type and burner arrangement;
- load pattern;

TABLE 4. PRIMARY SULFATE EMISSION FACTORS UTILIZED FOR WG 3B EMISSIONS ESTIMATES

Source category	NEDS source classification codes (SCC)	Normalized primary sulfate emission factors
Electric Utilities		
Coal (1.7-2.64% S content)	1-01-001 through 1-01-003	0.456 lbs/ton
Residual oil (1.75-2.25% S content)	1-01-004	9.143 lbs/1,000 gallons
Distillate oil (0.3% S content)	1-01-005	11.808 lbs/1,000 gallons
Non-Utility Coal (2.2% S content)	1-02-001 through 1-02-002	0.608 lbs/ton
	1-02-003	0.480 lbs/ton
	1-03-001 through 1-03-002	0.608 lbs/ton
	1-03-003	0.480 lbs/ton
Industrial Oil (0.3% S content)	1-02-005	11.808 lbs/1,000 gallons
Commercial Oil (0.3% S content)	1-03-005	12.960 lbs/1,000 gallons
Residential Oil (0.3% S content)	1-05-002	15.552 lbs/1,000 gallons
Primary Copper Smelters	3-03-005-1	22.500 lbs/ton concentrated ore
	3-03-005-2	1.080 lbs/ton concentrated ore
	3-03-005-3	5.760 lbs/ton concentrated ore
	3-03-005-4	15.660 lbs/ton concentrated ore
Primary Zinc Smelters	3-03-030	55.500 lbs/ton processed

(continued)

TABLE 4. (continued)

Source category	NEDS source classification codes (SCC)	Normalized primary sulfate emission factors
Primary Aluminum Smelters	3-04-001	0.5% of SO_2
Iron/Steel Sintering	3-03-008	2% of SO_2
Coke	3-03-003	0.328 lbs/ton coal charged
Sulfuric Acid	3-01-023	0.100 lbs/ton acid produced
Kraft Pulp Mill	3-07-001	*
Sulfite Pulp Mils	3-07-002	†
Cement Plants	3-05-006 through 3-05-007	§
Gypsum Plants	3-05-015	#
Sulfur Recovery Claus Plants	3-01-032	2.8 lbs/ton produced
Catalytic Cracking Units	3-06-002	15.0 lbs/1,000 barrels fuel

* Total sulfate emissions for kraft pulp mills estimated as 85 percent of NEDS total particulate emissions from kraft recovery boilers.

† Total sulfate emissions from sodium-base sulfite mills estimated as 70 percent of NEDS SO_2 emissions; for calcium-base sulfite mills estimated as 25 percent of NEDS SO_2 emissions.

§ Total sulfate emissions from cement kilns estimated as 5.6 lb/ton of cement on an uncontrolled basis. Average particulate control efficiency from NEDS data assumed to apply in order to calculate actual emissions.

Total sulfate from gypsum plants estimated as 56 percent of NEDS actual particulate emissions.

- emission control system;
- operating status (e.g., retirement, emergency only); and
- fuel characteristics.

The units selected for testing were grouped according to the following age categories:

Group I: 25 years or older;

Group II: 10 to 25 years old; and

Group III: less than 10 years old.

The relative size of the units in these age categories was similar. Group I ranged from 69 to 215 MW (113 MW average); Group II from 150 to 225 MW (192 MW average); and Group III from 227 to 610 MW (469 MW average). For the purposes of the test program, one unit was selected from Group I and two units each were selected from Groups II and III. One unit from Group II and one from Group III are equipped with control devices for controlling particulate emissions only. The other two units in Groups II and III are equipped with full particulate and SO_2 control devices.

The unit tested from Plant A has a rated nameplate generating capacity of 560 MW and was placed into service in 1970. This Babcock and Wilcox unit has an opposed-fired burner configuration and is equipped with a Buell weighted wire electrostatic precipitator to control particulate emissions.

The unit for Plant B which was selected from Group I has a rated nameplate generating capacity of 125 MW and was placed into service in 1954. This Babcock and Wilcox unit has a front-fired burner configuration and is equipped with a retrofit Research Cottrell ESP installed in 1973 to control particulate emissions.

The Plant C unit, which was selected from Group II, has a rated nameplate generating capacity of 163 MW and was placed into service in 1958. This Combustion Engineering unit has a tangential-fired burner configuration. The particulate emission control system consists of two ESP's in series. The newer retrofit Research Cottrell ESP was installed in 1975.

A unit was selected at Plant D to represent Group III. The unit tested has a rated nameplate generating capacity of 411 MW and was placed into service in 1978. This Babcock and Wilcox unit has an opposed-fired burner configuration. The air pollution control equipment consists of an American Air Filter (AAF) rigid frame ESP that was installed in 1978. After passing through the ESP, the flue gas enters a carbide lime mobile bed flue gas desulfurization (FGD) system which was also installed in 1978 by AAF.

The unit at Plant E from Group II has a rated nameplate generating capacity of 156 MW and was placed into service in 1962. This Combustion Engineering unit has a horizontal-fired burner configuration. The air pollution control equipment consists of a Research Cottrell weighted wire ESP installed in 1962. After passing through the ESP, the flue gas enters an AAF lime slurry FGD system which was installed in 1976.

During onsite testing, the units were operated in a normal manner with the loads changing according to demand. Tests were conducted over a 5-day sampling period in an effort to obtain emission data under a number of operating conditions. The Controlled Condensation System (CCS) was utilized to simultaneously collect and differentiate particulate sulfate, H_2SO_4, and SO_2. Two CCS samples were collected each day over the five day testing period. Table 5 summarizes the primary sulfate emission factors calculated from the source measurements taken at each unit.

PRIMARY SULFATE EMISSIONS FROM A LIGNITE AND A WESTERN BITUMINOUS COAL-FIRED UTILITY SOURCE[26]

The purpose of the study was to provide background data on the sulfur dioxide and primary sulfate emissions from power plants burning North Dakota lignite, and Western coal. The two plants tested were the Leland Olds Steam Plant of the Basin Electric Company, Stanton, North Dakota, and the Sherburne County (Sherco) generating plant of North States Power Company, Becker, Minnesota.

The unit tested at the Leland Olds Station is sized at 440 MW and went into commercial operation in December 1975. The unit is a Babcock and Wilcox cyclone-fired boiler with a rated steam capacity of 3,000,000 lb/hour. A Joy Manufacturing Company electrostatic precipitator provides a design particulate

TABLE 5. PRIMARY SULFATE EMISSION FACTORS FOR BITUMINOUS COAL-FIRED UTILITY SOURCES

Group	Plant	Size (MW)	Fuel sulfur content (weight %)	Emissions controls	Normalized primary sulfate emission factor (lbs/ton)
I	B	125	0.9	ESP	0.293
II	C	163	0.9	ESP	0.296
	E	156	3.3	ESP	0.381
	E	156	3.3	ESP and FGD*	0.269
III	A	560	1.0	ESP	0.162
	D	411	3.5	ESP and FGD	0.279

* FGD sulfate removal efficiency = 29.4 percent.

removal efficiency of 99.5 percent. During the tests, the unit was burning a North Dakota lignite with a dry heating value of 10,515 Btu/lb containing 1.38 weight percent sulfur. Primary sulfate emissions were determined using EPA Modified Method 6.

The unit tested at the Sherco plant was sized at 700 MW and employed a Combustion Engineering controlled circulation, single-reheat, balanced draft steam generator. The emission control utilizes a Combustion Engineering scrubber system which is a tail-end limestone, negative pressure, two-stage wet scrubber. A rod venturi is used as the first stage for particulate removal and a marble bed as the second stage for sulfur dioxide removal. The complete scrubber consists of 12 modules, 11 of which are required for full load operation. When tested, the unit was burning a Western bituminous coal with a dry heating value of 11,649 Btu/lb containing 1.10 percent sulfur. Samples were collected at both the inlet and outlet of a representative scrubber module. Primary sulfate emission measurements were made using EPA Modified Method 6.

Table 6 summarizes the primary sulfate emission factors calculated for both units tested during the program. The scrubber inlet sulfate emissions measured at Sherco were taken prior to any particulate removal.

MEASUREMENT OF SULFATE EMISSIONS AT KCP&L HAWTHORNE STATION, KANSAS CITY, MISSOURI[27]

The objectives of the testing included obtaining measurements data on total water-soluble sulfates emitted from a power plant burning a mixture of Chelsea (Oklahoma) and Wyoming coals. The unit tested was built in 1969 by Combustion Engineering as a corner-fired boiler. It has six coal feeders and the entire boiler system is under positive pressure. The boiler is rated for 468 MW and uses two Buell Engineering electrostatic precipitators in series with a design load of 400 MW. During operation, two of the coal feeders use a high-sulfur Oklahoma coal with the remaining four fed with low-sulfur Wyoming coal. Total sulfate emission samples were collected at the breaching of the stack after the precipitators using EPA Modified Method 6. Table 7 summarizes the calculated primary sulfate emission factor derived from the source

TABLE 6. PRIMARY SULFATE EMISSION FACTORS FOR A LIGNITE AND A WESTERN BITUMINOUS COAL-FIRED UTILITY SOURCE

Unit size	Fuel sulfur content	Emissions controls	Normalized primary sulfate emission factor (lbs/ton)
440 MW	1.38 weight % (Lignite)	ESP	1.951
700 MW	1.10 weight % (Western Bituminous)	(None)	1.627
700 MW	1.10 weight % (Western Bituminous)	FGD*	0.761

* FGD sulfate removal efficiency = 53 percent.

TABLE 7. PRIMARY SULFATE EMISSION FACTORS FOR A MIXED BITUMINOUS COAL-FIRED UTILITY BOILER

Unit size	Fuel sulfur content	Emissions controls	Normalized primary sulfate emission factor (lbs/ton)
468 MW	1.67 weight %*	ESP	1.290

* Based on "as-fired" mixture of 1.37 percent Wyoming coal and 2.19 percent Oklahoma coal.

measurements. The normalized emission factor represents sulfate emissions for the particular ratio of high and low sulfur coals that were being used during the testing.

CCEA -- SULFATES SAMPLING AND ANALYSIS ON A UTILITY FGD UNIT[28]

The controlled-condensation system was used to collect reactive sulfur species at the inlet and outlet of the FGD unit on Columbus and Southern Ohio Electric's Conesville Power Station. The Conesville Power Station is a 2,055 MW six-unit, coal-fired facility located on the Muskingum River near Coshocton, Ohio. Tests were conducted on Unit 5 which is equipped with an FGD system. The unit is a coal-fired, dry bottom Combustion Engineering steam generator rated at 411 MW. The fuel is a blend of high-sulfur Ohio coals containing approximately 4.7 percent sulfur and 15 percent ash. The air pollution control system consists of a cold-side electrostatic precipitator by Research-Cottrell and a Universal Oil Products/Air Correction Division sulfur dioxide scrubber. The precipitator is designed for 99.65 percent particulate removal. The turbulent contact SO_2 absorber module is designed for an SO_2 removal efficiency of 89.6 percent.

Gas samples were taken at the inlet and outlet of the FGD module using the controlled-condensation sampling and analysis method. Table 8 summarizes the calculated primary sulfate emission factors for the source with and without FGD controls.

PRIMARY SULFATE EMISSIONS FROM RESIDUAL OIL-FIRED BOILERS[29]

A specific point source of sulfate emissions was chosen in the Northeastern United States to assess the impact of sulfate emissions on air quality. A comprehensive particulate and sulfur emission characterization was performed at the Albany Steam Station, owned and operated by the Niagara Mohawk Power Corporation in Glenmont, New York.

Each of four boilers at the plant is a Combustion Engineering unit wth tangential combustion, rated at 675,000 lbs steam/hour and 100 MW net power output. During the period of study, the plant was firing residual fuel oil of Venezuelan origin with an approximate heating value of 18,600 Btu/lb. The

TABLE 8. PRIMARY SULFATE EMISSION FACTOR FOR A BITUMINOUS COAL-FIRED UTILITY SOURCE

Unit size	Fuel sulfur content	Emissions controls	Normalized primary sulfate emission factor (lbs/ton)
411 MW	4.7 weight %	ESP	0.793
		ESP and FGD*	0.480

* FGD sulfate removal efficiency = 39.5%.

average sulfur content was 1.0 percent with vanadium and ash concentrations of 200 ppm and 0.12 percent , respectively. A fuel additive, consisting of magnesium and magnesium oxide in a petroleum liquid, was added to the oil just prior to combustion to inhibit corrosion caused by sulfuric acid. The additive was injected into the fuel oil feed lines at a nominal ratio of 2,500:1 (oil, additive by volumetric measure).

The boilers were operated at an average of 80 percent maximum generation capacity during the measurement period. Each boiler exhaust is vented to an individual stack. Three of the four boiler exhaust stacks were sampled for primary sulfate emissions using the controlled condensation sampling and analysis method. The calculated primary sulfate emission factors for each of the units is summarized in Table 9.

PRIMARY SULFATE EMISSIONS FROM A COAL AND OIL-FIRED INDUSTRIAL BOILER WITH FGD CONTROLS[30]

The study was designed to provide a comparative multimedia assessment of coal-firing and oil-firing in an industrial boiler. The boiler is an integral furnace, once-through, Babcock and Wilcox unit which was installed in 1958. In 1967, the unit was converted to fire either coal or oil with a 10 MW equivalent generating capacity.

The flue gases are treated by an air pollution system which consists of multicone units and a pilot FGD unit. The multiclones are the primary particulate control device. All of the flue gas passes through the multiclones after which the steam is split and two-thirds of the flue gas is ducted to the stack. The other one-third is ducted to the pilot FGD system which removes SO_2 and additional particulate matter.

The flue gas desulfurization (FGD) system was designed and manufactured by FMC Corporation. The process utilizes a sodium sulfite-sodium bisulfite solution as the absorbent.

A high volatile bituminous feed coal was utilized for all coal-fired tests. The coal contained 1.64 weight percent sulfur with a heating value of 12,683 Btu/pound. Simultaneous primary sulfate emission measurements were made simultaneously at the inlet and outlet of the FGD unit using the controlled condensation sampling and analysis method.

TABLE 9. PRIMARY SULFATE EMISSION FACTORS FOR RESIDUAL OIL-FIRED UTILITY BOILERS

Unit	Size (MW)	Fuel sulfur content (weight %)	Emissions controls	Normalized primary sulfate emission factor (lbs/1,000 gallons)
1	100	1.88	Magnesium fuel oil additive	5.089
2	100	1.72	Magnesium fuel oil additive	5.589
4	100	1.45	Magnesium fuel oil additive	5.640

Oil-fired tests were conducted with the unit fired with a No. 6 residual fuel oil containing 1.96 weight percent sulfur and a heating value of approximately 16,600 Btu/pound. The fuel vanadium content was approximately 36.5 ppm. During the tests, the furnace exit oxygen content averaged about 3.5 percent. Primary sulfate emission measurements were conducted simultaneously at the inlet and outlet of the FGD using the controlled condensation sampling and analysis method.

Table 10 summarizes the calculated primary sulfate emission factors for the unit burning either coal or oil. Emission factors have been calculated for the unit operating with or without the FGD system by assuming that the FGD inlet concentrations approximate the atmospheric emissions from the boiler in the absence of sulfur dioxide controls.

PRIMARY SULFATE EMISSIONS FROM A DRY BOTTOM INDUSTRIAL BOILER FIRING PULVERIZED BITUMINOUS COAL[31]

The study includes an assessment of the potential impact of air emissions, wastewater effluents, and solid wastes resulting from the operation of dry bottom industrial boilers firing pulverized bituminous coal. Consuming approximately 23 million metric tons of such coal per year, this source category constitutes the primary method of firing coal in industrial boilers.

The boiler chosen for sampling and analysis was a horizontally-fired, dry bottom unit burning pulverized Appalachian bituminous coal to produce steam for process and space heating at an industrial site. The boiler has a rated firing capacity of 123 MBtu/hour and an output capacity of 100,000 lbs steam/hour. The air emissions from the unit are controlled by a high efficiency electrostatic precipitator. The coal burned has an as received heating value of 28.78 MJ/kg and a sulfur content of 0.91 percent.

Air emission samples were collected at the outlet duct of the ESP using a modified EPA Method 8 procedure. Table 11 summarizes the calculated primary sulfate emission factor for the unit.

TABLE 10. PRIMARY SULFATE EMISSION FACTORS FOR A BITUMINOUS COAL OR RESIDUAL OIL-FIRED INDUSTRIAL BOILER WITH FGD

Fuel type	Fuel sulfur content	Emissions controls	Normalized primary sulfate emission factor
Bituminous coal	1.64 weight %	Multiclone	2.646 lbs/ton
	1.64 weight %	Multiclone and FGD	0.462 lbs/ton
Residual oil	1.96 weight %	Multiclone	5.296 lbs/1,000 gallons
	1.96 weight %	Multiclone and FGD	2.616 lbs/1,000 gallons

TABLE 11. PRIMARY SULFATE EMISSION FACTOR FOR A COAL-FIRED DRY BOTTOM INDUSTRIAL BOILER

Fuel type	Fuel sulfur content	Emissions controls	Normalized primary sulfate emission factor (lbs/ton)
Appalachian coal	0.91 weight %	ESP	0.199

PRIMARY SULFATE EMISSIONS FROM LOW-SULFUR RESIDUAL OIL-FIRED COMMERCIAL AND INSTITUTIONAL BOILERS[32]

The study involved the measurement of primary sulfate emissions from four non-industrial packaged boilers located in the New York, NY metropolitan area. All units tested were burning a 0.3 percent sulfur hydrodesulfurized residual fuel oil.

Boiler No. 1 was at the Starrett City residential apartment complex in Brooklyn, New York which generates its electricity, heating, and cooling requirements by a central power complex. The power station centers around four boilers, each rated at 110,000 lbs/hour steam, at a firing rate of 7,850 lbs/hour of fuel oil. The design primary fuel is natural gas, but due to economic and availability considerations, the units have been operated on No. 6 fuel oil. Testing was done on the No. 4 boiler, a Combustion Engineering Type 28-VP-12W constructed in 1971, rated at 110,000 lbs/hour steam. During the tests, a No. 6 residual fuel oil with a rated sulfur content of less than 0.3 percent was used as the sole fuel source.

Boiler No. 2 was located at Long Island University in Brooklyn, New York. Steam requirements for the university building complex are supplied by three Compak Water Tube Generators, Model FPL-21-600, manufactured by the International Boiler Works Company. Each unit is rated at 24,000 lbs/hour steam. Emission tests were run on the outlet of the No. 3 boiler. The fuel used was a No. 4 low-sulfur oil. During all test periods, the boiler was on lead status and was to run continuously at uniform load conditions.

Testing was conducted at Boiler 3 which is located at the Columbia Presbyterian Hospital in New York, NY. Five boilers supply the steam needs, two Combustion Engineering and one Babcock and Wilcox units rated at 120,000 lbs/hour steam, and two Babcock and Wilcox units rated at 45,000 lbs/hour steam. The units are fired with a No. 6, low sulfur oil with Gilbert Fire-Side Additive continuously injected to the oil. All emission tests were run on the No. 3 Babcock and Wilcox boiler, rated at 120,000 lbs/hour steam at 250 psig built in 1975.

Boiler No. 4 (a confidential source in New York, NY) is rated at 125,000 lbs/hour steam at 300 psig. The fuel burned during all tests was a No. 6 low-sulfur residual oil.

TABLE 12. PRIMARY SULFATE EMISSIONS FROM RESIDENTIAL/INSTITUTIONAL BOILERS BURNING LOW-SULFUR RESIDUAL OIL

Unit	Size (lb/hr steam)	Fuel sulfur content (weight %)	Emissions controls	Normalized primary sulfate emission factor (lbs/1,000 gallons)
1	110,000	0.3	None	21.55
2	24,000	0.3	None	19.20
3	120,000	0.3	Fuel oil additive	35.47
4	125,000	0.3	None	24.07

All primary sulfate emission measurements were made using the modified EPA Method 6 sampling and analysis procedure. Table 12 summarizes the calculated primary sulfate emission factors for the four boilers tested during the study.

PRIMARY SULFATE EMISSIONS FROM A BARK/COAL-FIRED BOILER[33]

A three week monitoring study was carried out to assess the impact of stationary source emissions from a typical pulp and paper mill on local ambient air quality. Primary sulfate emission measurements were taken at a coal/wood bark-fired boiler at the mill.

The unit is a Riley bark boiler which is a combination stoker coal- and bark-fired boiler which is used for supplemental power generation. Typical steam production is about 80 tons/hour which is achieved by burning a steady stream of bark from the chipping operation. Coal is fed by a chute as a supplemental fuel in order to maintain load. The unit is equipped with primary and secondary Corn multiclone mechanical collectors and a venturi scrubber.

During the measurements, the unit was fired with about 29 tons/hour of bark with an average sulfur content of 0.1 percent along with about 1 ton/hour of coal. A series of seven primary sulfate emission measurements were made using the controlled condensation sampling and analysis method. Table 13 summarizes the normalized primary sulfate emission factor for the unit.

PRIMARY SULFATE EMISSIONS FROM OIL-FIRED RESIDENTIAL HEATING SOURCES[34]

During the study, emissions from gas- and oil-fired residential heating sources were assessed through a critical examination of existing emissions data, followed by the conduct of a phased measurement program to fill gaps in the emissions data base. Particulate sulfate, SO_2, and SO_3 emission data were obtained at two of the oil-fired sites. The choice of the specific sites in the program was based on the representativeness of the sites as measured against important characteristics of systems within each source category such as:

- burner type and age;
- firing rate; and
- duty cycle.

TABLE 13. PRIMARY SULFATE EMISSION FACTOR FOR A WOOD BARK- AND COAL-FIRED BOILER

Mixed-fuel type	Combustion fuel sulfur content	Emissions controls	Normalized primary sulfate emission factor
Wood bark (96%) Coal (4%)	0.1 weight %	Dual multiclone and venturi	3.6 lbs/ton

One of the oil-fired residential combustion units tested as an Arcoliner No. W.O. 351, Series 3AS3 unit with a conventional high pressure burner using a forced air heating medium with a rated capacity of 141,000 Btu/hour. The unit tested was 16 years old.

The second unit tested was an Armstrong, Model L61-95 A527 device with a conventional high pressure burner. The unit, approximately six years old, was rated at 120,000 Btu/hour and employed a forced air heating medium.

Both units were burning a distillate fuel oil containing approximately 0.25 percent sulfur. The controlled condensation sampling and analysis method was used to collect two samples from the emissions of each unit. Table 14 summarizes the calculated primary sulfate emission factors based on the emission measurements.

PRIMARY SULFATE EMISSIONS AT A SCRUBBER-EQUIPPED COAL-FIRED BOILER[35]

The controlled condensation sampling and analysis method was used to evaluate the performance of two prototype sulfuric acid monitors at a coal-fired boiler employing FGD. The testing was done at the Widows Creek Steam Plant Unit No. 8 operated by the Tennessee Valley Authority at Bridgeport, Alabama. The unit is a 300 MW balanced draft, tangentially-fired coal boiler burning a 4.3 percent sulfur coal. TVA retrofitted this unit with a limestone FGD system with a designed SO_2 removal efficiency of 80 percent. The emission control system consists of an electrostatic precipitator followed by four variable-throat venturi scrubber/multi-grid tower absorber trains containing one packed tower.

Sampling was conducted at the outlet of Module A. Table 15 contains the normalized primary sulfate emission factor calculated from the measurements data.

TABLE 14. PRIMARY SULFATE EMISSION FACTORS FOR DISTILLATE OIL-FIRED RESIDENTIAL HEATING SOURCES

Unit	Heating rate (Btu/hr)	Age	Fuel sulfur content (weight %)	Normalized primary sulfate emissions factor (lbs/1,000 gallons)
Arcoliner Series No. W.O. 351, 3AS3	141,000	16 years	0.25	7.09
Armstrong L61-95 A527	120,000	6 years	0.25	4.21

TABLE 15. PRIMARY SULFATE EMISSION FACTORS FOR A SCRUBBER EQUIPPED COAL-FIRED BOILER

Unit size	Fuel sulfur content	Emissions controls	Normalized primary sulfate emissions factor
300 MW	4.3 wt. % butuminous	ESP and FGD	0.005 lbs/ton

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